Geological Survey of Canada

CURRENT RESEARCH
2003-H2

A method to determine electrode polarization characteristics

T.J. Katsube and N. Scromeda-Perez

2003

CURRENT RESEARCH

Natural Resources Canada | Ressources naturelles Canada

Canada

106-03645/

©Her Majesty the Queen in Right of Canada 2003
ISSN 1701-4387

Available in Canada from the
Geological Survey of Canada Bookstore website at:
http://www.nrcan.gc.ca/gsc/bookstore (Toll-free: 1-888-252-4301)

A copy of this publication is also available for reference by depository
libraries across Canada through access to the Depository Services Program's
website at http://dsp-psd.pwgsc.gc.ca

All requests for permission to reproduce this work, in whole or in part, for purposes of commercial use, resale, or redistribution shall be addressed to: Earth Sciences Sector Information Division, Room 402, 601 Booth Street, Ottawa, Ontario K1A 0E8.

Author's address

T.J. Katsube *(jkatsube@nrcan.gc.ca)*
N. Scromeda-Perez *(nperez@nrcan.gc.ca)*
Geological Survey of Canada
601 Booth Street
Ottawa, Ontario K1A 0E8

Publication approved by Mineral Resources Division

A method to determine electrode polarization characteristics

T.J. Katsube and N. Scromeda-Perez

Katsube, T.J. and Scromeda-Perez, N., 2003: A method to determine electrode polarization characteristics; Geological Survey of Canada, Current Research 2003-H2, 7 p.

Abstract: Spectral induced polarization (spectral-IP) characteristics of pairs of graphite electrodes have been measured to determine the capacitance characteristics of the electrochemical double layers on their surfaces. The purpose was to establish a method to determine these characteristics so that the electrode effects could be subtracted from spectral-IP measurements of rock or soil samples, using a two-electrode system. Whereas four-electrode systems automatically eliminate such effects, complications develop when wide frequency ranges or varied pressure systems are used, and when textural elements of the electrical mechanisms in rocks and soils are studied.

Electrode characteristics are represented by capacitance over electrode surface area (C_E/A) and its frequency dependence coefficient (α_E). Results indicate that C_E/A and α_E display ranges of 1.06×10^{-4} to 4.98×10^{-4} F/cm^2 and 0.181 to 0.360, respectively, and that the repeatability of these values is required to increase the efficiency and accuracy of spectral-IP measurement.

Résumé : Les caractéristiques de paires d'électrodes en graphite utilisées en polarisation provoquée spectrale (PP spectrale) ont été mesurées afin de déterminer les caractéristiques capacitives de la double couche électrochimique présente à la surface de celles-ci. Ces mesures avaient pour objet l'établissement d'une méthode de détermination de ces caractéristiques afin que les effets d'électrode puissent être soustraits des mesures de PP spectrale effectuées sur des échantillons de roche ou de sol au moyen d'un système à deux électrodes. Alors que les systèmes à quatre électrodes permettent d'éliminer automatiquement ces effets, des complications se manifestent lorsque des plages étendues de fréquences ou des systèmes à pression variable sont utilisés, ou encore lorsque l'on veut étudier les composantes texturales du mécanisme électrique dans les roches et les sols.

Les caractéristiques des électrodes sont exprimées à l'aide de la capacitance en fonction de la surface de contact de l'électrode (C_E/A) et d'un coefficient relatif à la fréquence (α_E). Les résultats obtenus révèlent que les valeurs de C_E/A varient de $1,06 \times 10^{-4}$ à $4,98 \times 10^{-4}$ F/cm^2 et celles de α_E ,de 0,181 à 0,360. En outre, il est nécessaire que la répétitivité de ces résultats soit vérifiée si l'on veut augmenter l'efficacité et la précision des mesures de PP spectrale.

INTRODUCTION

The spectral induced polarization (spectral-IP) characteristics of pairs of graphite electrodes, of several different diameters, have been measured in order to determine the permittivity or capacitance characteristics of their electrochemical double layers. A four-electrode system is often used for laboratory electrical measurements of rock or soil samples. However, this electrode arrangement causes complications for measurements at varied frequencies or confining pressures, and makes it difficult to study the effect of different rock-forming components. For such cases, a two-electrode sample-holder system is favoured. This system, however, introduces unwanted electrode effects under certain conditions, such as for low-resistivity samples. Usually, a certain frequency can be chosen to avoid the electrode effects, but only for single frequency measurements. High-resistivity samples do not cause a problem of this nature. Therefore, for two-electrode sample-holder systems to cover wide frequency, confining-pressure, and sample-resistivity ranges, it is necessary to subtract the electrode-capacitance effect. The purpose of this study is to test a method to determine the electrode electrochemical double-layer permittivity or capacitance values. This paper describes the theory, method of investigation, and experimental results, and discusses the accuracy of these results as a means of subtracting the electrode-capacitance effects.

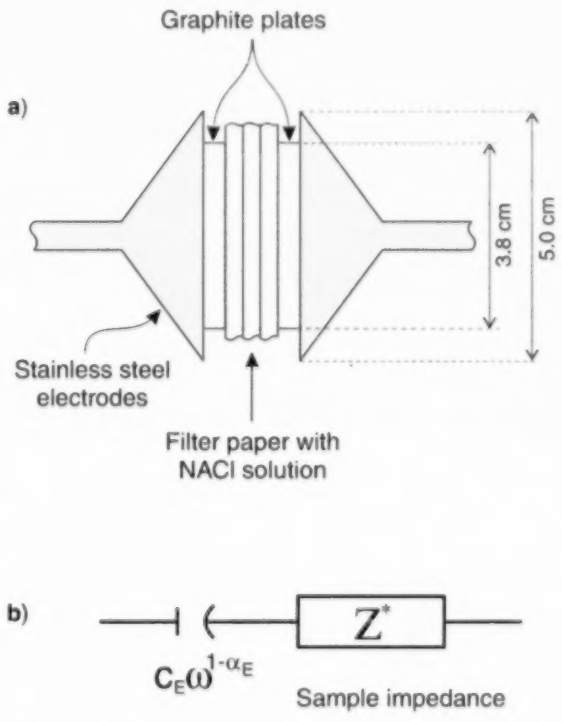

Figure 1. *a) Two-electrode sample-holder system used in this study, and* ***b)*** *equivalent circuit of this system (Katsube, 2001). C_E is the electrode capacitance (graphite plate).*

METHOD OF INVESTIGATION

Sample holder and measuring system

The sample holder and measuring system used to obtain the data have been frequently described elsewhere (e.g. Katsube, 1975; Gauvreau and Katsube, 1975; Katsube and Walsh, 1987; Katsube and Salisbury, 1991). The sample holder is a two-electrode system with stainless-steel electrodes and with graphite plates placed between these electrodes and the sample, as shown in Figure 1a (Katsube, 2001). The sample, in our case, is a set of 1 to 3 layers of filter paper saturated with 0.01N NaCl solution. The equivalent circuit of this system is shown in Figure 1b and is expressed as

$$Z^* = Z_F - jX_E, \tag{1a}$$

$$Z^+ = (Z_F^2 + X_E^2)^{1/2}, \tag{1b}$$

where Z^* and Z^+ are the complex impedance and the complex-impedance amplitude of the electrode and filter-paper layers respectively, Z_F is the impedance of the filter-paper layers, X_E is the reactance of the graphite-electrode surfaces, and j is the root of -1. This X_E is expressed by

$$X_E = 1/(C_E\omega^{1-\alpha E}), \tag{2}$$

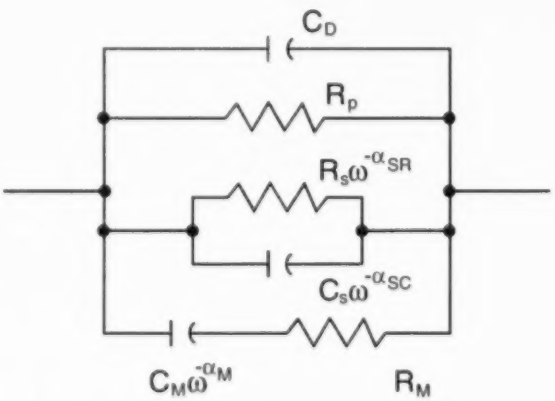

Figure 2. *Equivalent circuit for anisotropic mineralized rock (Katsube, 2001). C_D is the capacitance due to the dielectric characteristics of the rock; R_P is the resistance to the electrical current flow through the pores of the nonmineralized layer; and $R_s\omega^{-\alpha SR}$ and $C_S\omega^{-\alpha SC}$ are the frequency-dependent resistance and capacitance of the pore surfaces in the nonmineralized layer, where α_{SR} and α_{SC} are coefficients and ω is the angular frequency. R_M and $C_M\omega^{-\alpha M}$ are the resistance and frequency-dependent capacitance, respectively, of the mineralized layers and α_M is a coefficient.*

Table 1. Results of Z', Z", and Z⁺ over a frequency range of 1 to 10^6 Hz for graphite electrodes #1d, #2f and #3a, measured with one layer of filter paper saturated in 0.01 N NaCl.

Frequency (Hz)	#1d $C_E/A = 1.342 \times 10^{-4}$ F/cm² $\alpha_E = 0.197$ $r_D = 5.74$ cm			#2f $C_E/A = 2.823 \times 10^{-4}$ F/cm² $\alpha_E = 0.238$ $r_D = 3.77$ cm			#3a $C_E/A = 3.758 \times 10^{-4}$ $\alpha_E = 0.250$ $r_D = 3.13$ cm		
	Z⁺ (W)	Z' (W)	Z" (W)	Z⁺ (W)	Z' (W)	Z" (W)	Z⁺ (W)	Z' (W)	Z" (W)
1	69.39	21.7	65.9	86.06	35.4	78.4	108.79	59.0	91.4
1.6	47.62	17.4	44.3	61.05	29.2	53.6	80.79	50.7	62.9
2.5	33.00	13.9	29.9	44.47	24.8	36.9	62.34	44.7	43.4
4.0	23.43	11.7	20.3	33.41	21.5	25.6	50.52	40.5	30.2
6.3	17.17	10.1	13.9	26.11	19.1	17.8	43.02	37.5	21.1
10	13.09	8.88	9.63	21.33	17.2	12.6	38.26	35.2	14.9
16	10.40	7.94	6.72	18.18	15.9	8.88	35.20	33.5	10.7
25	8.61	7.21	4.71	16.13	14.8	6.31	33.20	32.3	7.68
40	7.48	6.71	3.30	14.79	14.1	4.50	31.87	31.4	5.62
63	6.77	6.36	2.31	13.93	13.6	3.23	30.93	30.6	4.20
10^2	6.34	6.13	1.63	13.38	13.2	2.35	30.24	30.1	3.24
1.6×10^2	6.09	5.97	1.17	12.99	12.9	1.75	29.76	29.6	2.63
2.5×10^2	5.91	5.85	0.876	12.72	12.6	1.35	29.35	29.3	2.31
4.0×10^2	5.80	5.76	0.681	12.54	12.5	1.10	29.04	29.0	2.23
6.3×10^2	5.70	5.67	0.596	12.37	12.3	1.00	28.63	28.5	2.36
10^3	5.60	5.57	0.585	12.21	12.2	1.01	28.08	28.0	2.71
1.6×10^3	5.48	5.44	0.634	12.02	12.0	1.14	27.28	27.1	3.10
2.5×10^3	5.30	5.25	0.716	11.73	11.7	1.35	26.24	26.0	3.43
4.0×10^3	5.05	4.98	0.785	11.28	11.2	1.58	25.05	24.8	3.57
6.3×10^3	4.73	4.66	0.804	10.65	10.5	1.68	23.82	23.6	3.49
10^4	4.39	4.33	0.711	9.95	9.83	1.55	22.65	22.4	3.25
1.6×10^4	4.09	4.06	0.523	9.36	9.27	1.23	21.51	21.3	2.85
2.5×10^4	3.87	3.86	0.263	8.92	8.89	0.815	20.51	20.4	2.26
4.0×10^4	3.75	3.75	0.059	8.66	8.66	0.366	19.75	19.7	1.53
6.3×10^4	3.73	3.70	0.424	8.52	8.52	0.096	19.22	19.2	0.763
10^5	6.26	1.23	6.14	9.04	5.30	7.32	17.97	15.1	9.73
1.6×10^5	6.28	1.25	6.16	9.04	5.31	7.31	17.95	15.1	9.67
2.5×10^5	6.34	1.24	6.22	9.06	5.27	7.37	17.94	15.1	9.70
4.0×10^5	6.39	1.25	6.26	9.08	5.27	7.40	17.90	15.1	9.62
6.3×10^5	6.57	1.20	6.46	9.18	5.25	7.53	17.91	15.1	9.67
10^5	10.67	2.12	10.5	10.68	3.05	10.2	18.48	13.0	13.2

Z' = Real impedance
Z" = Imaginary impedance
Z⁺ = Complex impedance amplitude
C_E/A = Capacitance of graphite electrodes per cm²
α_E, coefficient
r_D, graphite-plate (electrode) diameter

where ω represents the angular frequency, α_E represents a coefficient, and C_E represents the electrode capacitance. In this case, C_E is the capacitance of the electrochemical double layers that form on the graphite-plate surfaces, which are in direct contact with the NaCl solution that saturates the filter paper. The angular frequency (ω) is expressed by

$$\omega = 2\pi f, \tag{3}$$

where f is the frequency. The stray and leakage capacitances of the sample-holder system are eliminated at the time of measurement (Katsube and Collett, 1973; Gauvreau and Katsube, 1975). The electrode permittivity, ε_E, expressed by

$$\varepsilon_E = C_E / A, \tag{4}$$

is used to represent the electrical characteristics of the electrodes, where A is the surface area of the electrode plate that is in contact with the solution in the filter paper.

The equivalent circuit for a sample, of which the impedance is represented by Z_F, is generally represented by Figure 2 (Katsube, 2001). In this case, our sample is a thin set of filter-paper layers, which makes most of the quantitative values of the parameters in the equivalent circuit irrelevant in comparison with that of the electrodes. The only parameter of importance in the circuit is R_P (resistivity of the fluid-pore system in a rock), which we will replace with R_F, the resistivity of the fluid-pore system of the filter-paper layers. This implies that, for our case

$$Z_F = R_F. \tag{5}$$

Table 2. Results of C_E/A and α_E determinations for 21 sets of graphite electrodes measured with one layer of filter paper saturated in 0.01 N NaCl.

Graphite Electrode Pair #	r_D (cm)	C_E/A ($F/cm^2 \times 10^{-4}$)	α_E
1a	5.74	1.06	0.230
1b	5.74	1.25	0.184
1c	5.74	1.60	0.181
1d	5.74	1.34	0.197
1e	5.74	2.20	0.200
1f	5.74	2.23	0.360
1g	5.74	2.05	0.230
2a	3.77	1.72	0.235
2b	3.77	3.11	0.251
2c	3.77	3.17	0.190
2d	3.77	1.56	0.220
2e	3.77	4.07	0.250
2f	3.77	2.82	0.238
3a	3.13	3.76	0.250
3b	3.13	4.98	0.280
3c	3.13	2.84	0.196
3d	3.13	5.08	0.220
3e	3.13	3.52	0.210
3f	3.13	5.36	0.240
3g	3.13	3.93	0.248
3h	3.13	2.71	0.225

C_E/A = Capacitance of graphite electrodes per cm^2
α_E = coefficient
r_D = diameter

This also implies that the impedance versus frequency (Z^+ vs. f) curves, expressed by Equation 1, will represent a simple series RC-circuit. That is, the Z^+ versus f curves will consist of a linearly decreasing segment and a constant segment, on a log-log scale, the former representing the electrode-capacitance effect of Equation 2. In order to determine C_E, we can take two measured values (Z_1 and Z_2) at two different frequencies (f_1 and f_2) on the linearly decreasing segment

$$Z_1 = 1/(C_E\omega_1^{1-\alpha E}), \quad (6a)$$

$$Z_2 = 1/(C_E\omega_2^{1-\alpha E}), \quad (6b)$$

and, first, determine α_E from Equations 6a and 6b

$$Z_1/Z_2 = (\omega_2/\omega_1)^{1-\alpha E}, \quad (7)$$

and then from

$$\alpha_E = 1 - [\log(Z_1/Z_2)]/[\log(\omega_2/\omega_1)]. \quad (8)$$

Since α_E is now known, we can insert it into either Equation 6a or 6b to derive C_E. We can now create Z versus f curves, expressed by the following equation using these derived values of α_E and C_E

$$Z_E = 1/(C_E\omega^{1-\alpha E}), \quad (9)$$

where Z_E represents the impedance of the electrode surfaces. These derived values of α_E and C_E can be refined by making minor changes to obtain a visual best fit between the curve created by Equation 9 and the linearly decreasing segment of the measured curve.

Sample Preparation and Measurement

Twenty-one pairs of graphite-plate electrodes were prepared by saturating them in de-ionized water (resistivity of 1.8×10^5 Ω•m), in order to rinse any contaminants from them. Seven pairs of electrodes have a diameter of 5.74 cm, six pairs have a diameter of 3.77 cm, and the remaining eight pairs have a diameter of 3.13 cm. Each of these seven, six and eight pairs of electrodes is a separate set of graphite plates that has seen a different amount of use in electrical measurements. Sheets of filter paper cut to the same diameter as the graphite electrodes were soaked in separate beakers with 0.01 N NaCl solution (resistivity of 7.71 Ω•m) prior to the measurements. First, one sheet of filter paper was placed between a pair of graphite electrodes (Figure 1a) and the electrical impedance measured over a frequency range of 1 to 10^6 Hz. The impedance measurement was repeated for each pair of electrodes using two and then three layers of filter paper soaked in 0.01 N NaCl solution. The filter-paper thickness was 0.012 cm per layer, implying that the electrode spacing varied from 0.012 to 0.036 cm for the one to three layers of filter paper.

EXPERIMENTAL RESULTS

Electrical impedance measurements, consisting of the real impedance (Z'), imaginary impedance (Z"), and complex-impedance amplitude (Z^+), were obtained for twenty-one pairs of graphite electrodes separated by one to three layers of filter paper saturated in 0.01 N NaCl. In these cases, Z' and Z" represent Z_F and X_E in Equation 1a, respectively. Results for three selected graphite electrode pairs are listed in Table 1. Measurements were made 24 hours after NaCl solution saturation of the filter-paper layers, to ensure that they represent impedance values that are stable with time. Under this state, it is expected that the NaCl solution has chemically equilibrated with all of the filter paper. Results of the capacitance per cm^2 (C_E/A) and coefficient (α_E) determinations for the graphite electrode pairs are listed in Table 2. Only the Z" versus f curves for the one filter-paper layer were used. The C_E/A and α_E values for the electrodes are in the ranges 1.063×10^{-4} to 4.980×10^{-4} F/cm^2 and 0.190 to 0.360, respectively.

Typical examples of complex-impedance amplitude (Z^+) plots, Z^+ as a function of frequency (f), are shown in Figure 3 for three pairs of graphite electrodes of different diameters separated by one to three layers of filter paper. Examples of imaginary impedance (Z") data plotted over a frequency range of 1 to 10^6 Hz for the same three pairs of graphite electrodes are shown in Figure 4. These curves show how Z" is affected by the different layers of filter paper. An example of

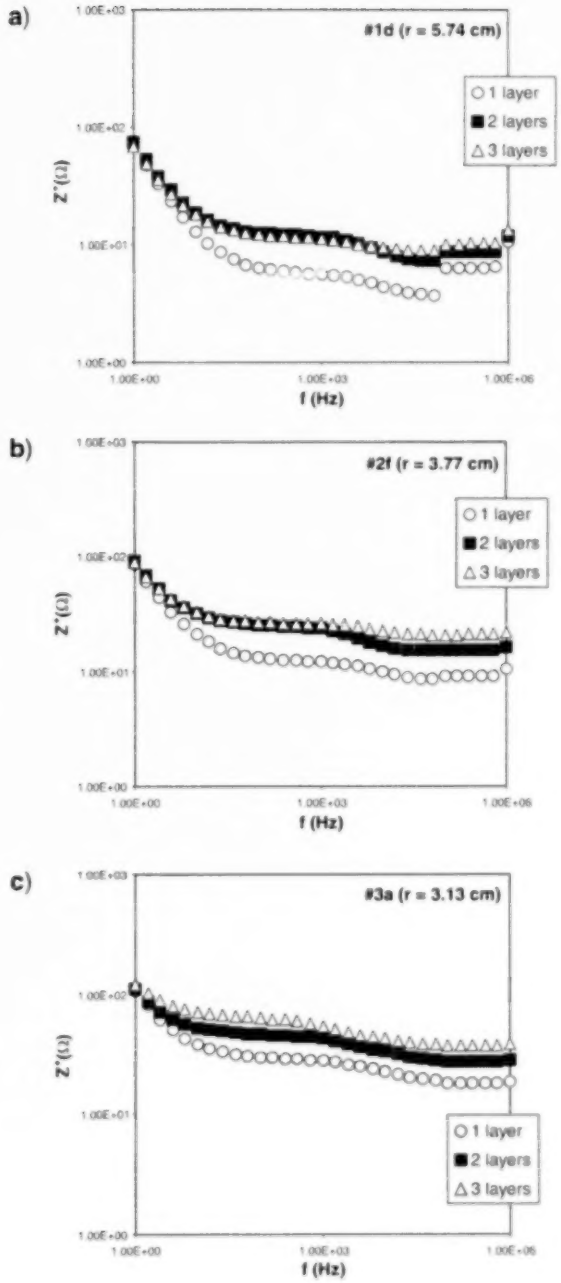

Figure 3. *Typical examples of complex-impedance amplitude (Z*) versus frequency (f) diagrams for the graphite electrodes separated by 1 to 3 layers of filter paper soaked in 0.01 N NaCl: **a)** graphite electrode pair #1d, diameter 5.74 cm; **b)** graphite electrode pair #2f, diameter 3.77 cm; and **c)** graphite electrode pair #3a, diameter 3.13 cm.*

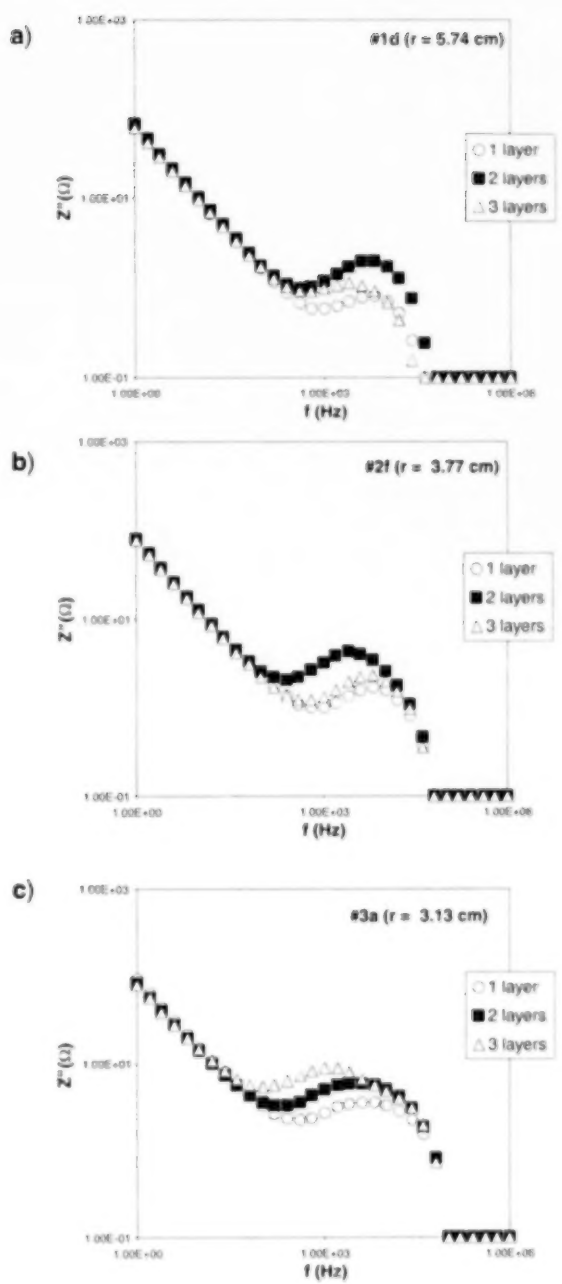

Figure 4. *Typical examples of imaginary impedance (Z") versus frequency (f) diagrams for the graphite electrodes separated by 1 to 3 layers of filter paper soaked in 0.01 N NaCl. **a)** graphite electrode pair #1d, diameter 5.74 cm; **b)** graphite electrode pair #2f, diameter 3.77 cm; and **c)** graphite electrode pair #3a, diameter 3.13 cm.*

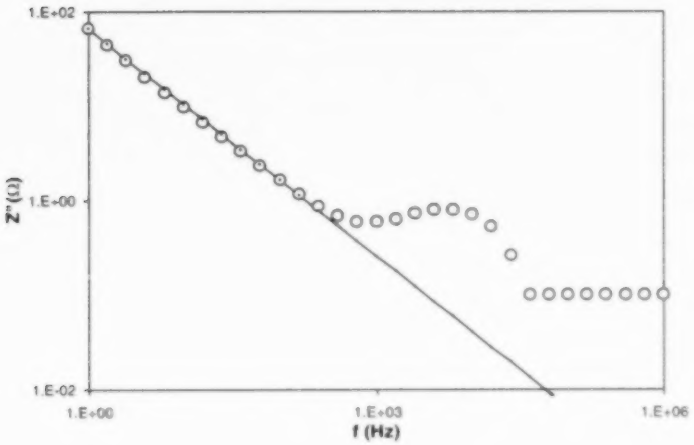

Figure 5.

Typical example of a Z_E versus f curve (solid line), calculated using Equation 9 and the derived values of α_E and C_E for graphite electrode pair #1d. Minor adjustments were made to these derived values in order to obtain a visual best fit with the linear section of the Z" versus f curve. The small circles are the actual measurements.

a Z" versus f curve, created from derived values of α_E and C_E using Equation 9, is displayed in Figure 5 for graphite electrode set #1d.

DISCUSSION AND CONCLUSIONS

The imaginary impedance versus frequency (Z" vs. f) curves in Figure 4 indicate that the frequency range of the linear section at the lower frequency end is sufficiently wide to select at least two (Z", f) points to determine the electrode capacitance (C_E) and its frequency dependence coefficient (α_E) values, with good accuracy, using Equations 6 to 8. The procedure for minor adjustments to the derived values of these two parameters, C_E and α_E, using the Z_E versus f curve (Equation 9) did not present any difficulties. As previously indicated, the results are compiled in Table 2, where electrode-capacitance values are represented by the capacitance per electrode surface area (C_E/A).

The Z^+ versus f curves (Fig. 3a–c) generally show an increase in Z^+ with increased number of filter-paper layers between the frequencies of 10 and 10^6 Hz, except for Figure 3c, in which the trend is slightly more complex. This general trend is expected from Equation 5. The trends for the Z" versus f curves in Figure 4 are considerably more complex, except for Figure 4c. This is likely due to the capacitance or permittivity effect of the filter-paper pore surfaces ($C_S\omega^{-\alpha SC}$; Fig. 2), which can complicate these curves. Also, the dielectric-constant effect of the filter paper (Fig. 2), not included in Equation 5, actually exists and causes the Z" values to decrease at the higher frequency end.

The C_E/A and α_E results (Table 2) display ranges of 1.06×10^{-4} to 4.98×10^{-4} F/cm^2 and 0.181 to 0.360, respectively. Whereas the maximum and minimum C_E/A values of this range are in the same order of magnitude, the difference between the two extreme values is too great to enable a single representative value to be assigned to the graphite electrode material for use in the laboratory spectral-IP measurements. That is, the C_E/A values for each specific pair of graphite electrodes must be known in order to eliminate the electrode effect from the spectral-IP measurements. This implies that the repeatability of the C_E/A values must also be known. In comparison, the α_E values display a considerably smaller range of variation. However, these values have a considerably larger effect on the spectral-IP measurements, compared to those of C_E/A, implying that they also should be known for each specific pair of graphite electrodes, in order to eliminate the electrode effect from the spectral-IP measurements.

The results of this study suggest that, in order to increase the efficiency and accuracy of spectral-IP measurement, further determinations of C_E/A and α_E should be carried out for comprehensive characterization of graphite electrode material. In addition, the repeatability of these characteristics should also be tested.

ACKNOWLEDGMENTS

The authors are grateful for the critical review of this paper and for the useful suggestions by T. Calvert. The authors also express their thanks to Susan Davis for producing the diagrams in this paper.

REFERENCES

Gauvreau, C. and Katsube, T.J.
1975 Automation in electrical rock property measurements; *in* Current Research, Part A, Geological Survey of Canada, Paper 75-1A, p. 83–86.

Katsube, T.J.
1975 The electrical polarization mechanism model for moist rocks, *in* Report of Activities, Part C, Geological Survey of Canada, Paper 75-1C, p. 353–360.
2001: An analytical procedure for determining spectral induced polarization characteristics of anisotropic rocks, Yellowknife mining district, Northwest Territories; Geological Survey of Canada, Current Research 2001-E3.

Katsube, T.J. and Collett, L.S.
1973: Measuring techniques for rocks with high permittivity and high loss; Geophysics, v. 38, p. 92–105.

Katsube, T.J. and Salisbury, M.
1991 Petrophysical characteristics of surface core samples from the Sudbury structure, *in* Current Research, Part E, Geological Survey of Canada, Paper 91-1E, p. 265–271.

Katsube, T.J. and Walsh, J.B.
1987 Effective aperture for fluid flow in microcracks, International Journal of Rock Mechanics and Mining Sciences and Geomechanics Abstracts, v. 24, p. 175–183.

Geological Survey of Canada Project 870057